



# Proterozoic Stromatolites and The Search for Life on Mars

Meredith E. Perry

University of Pennsylvania

NASA Ames Research Center

NASA Astrobiology Institute

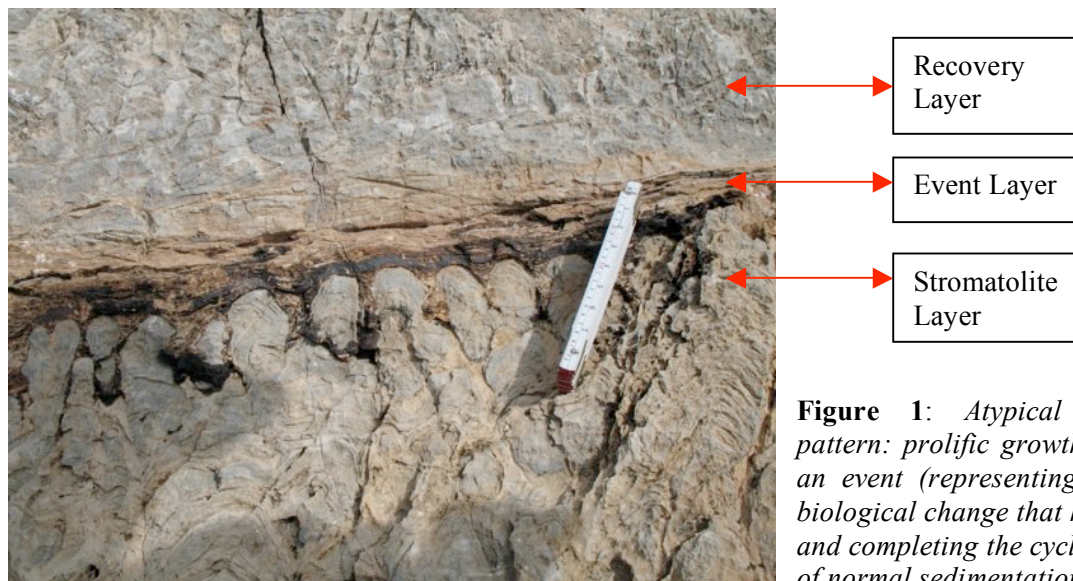
NASA Pennsylvania Space Grant Consortium

A place with a name that accurately describes its environment, Death Valley, CA is one of the most extreme environments on Earth. It's extremely dry, extremely hot, and extremely salty- and it is teeming with the only life that can thrive in these conditions: extremophiles. But this dry valley wasn't always a desert. In fact, a few billion years ago, this region was soaked in an ocean; a Paleozoic wet world that looked an awful lot like early Mars. A wetter Death Valley gave rise to lifeforms like cyanobacteria that have left their traces in the barren rock-face as ancient fossilized stromatolites. The extreme conditions and environmental history of Death Valley make it a suitable mars analogue site for study. Because Mars and Earth were environmentally comparable over similar time periods, lifeforms like stromatolites may have evolved similarly on mars during the same time period [McKay and Stoker, 1989]. Thus, Proterozoic stromatolites from the Death Valley region could be used as biosignatures analogous to possible fossilized Martian life on Mars. But before we can use these structures on Earth as models for Mars, a thorough understanding of the formation and functioning of Earth stromatolites is needed. Equally important, it is necessary to substantiate that the Martian structures interpreted as stromatolites really are of biogenic origin and were not produced by chemical and/or environmental processes.

In March 2010, NASA Ames Research Center scientist Christopher P. McKay, PhD, discovered a particularly odd section in the rock-face in the Mojave Desert that will help elucidate the nature of these extremophile stromatolites, and their environmental limits. Unique among formations from the Proterozoic, this Crystal Spring Formation has not been dolomitized and is still completely carbonate, as confirmed with Energy Dispersive Spectroscopy (EDS) and the hydrochloric acid method (research March 2010). Many carbonate sediments undergo dolomitization, which alters and distorts structures as magnesium replaces the original carbonate sediment. With the original carbonate sediment still intact and unaltered, there is a greater chance that the formation structures have been preserved - making the Crystal Spring Formation stromatolites one of the best examples of biogenic Proterozoic stromatolites.

The Crystal Spring Formation stromatolites were formed in a shallow lacustrine setting and have been radiometrically dated to 1.2-1.7 billion years old [Awramik *et al.*, 2000]. The section of interest contains repeated patterns of atypical stromatolite growth throughout the formation. These particular columnar stromatolites show repeated vertical growth sequences characterized by a layer of prolific growth followed by a geologic event represented by a dark layer with no stromatolites. This phase is followed by a layer of recovery with wavy laminae, and then the cycle repeats with another layer of columnar growth (Figure 1). The event layer clearly represents an environmental or biological change, which caused the subsequent stromatolite dormancy or extinction.

To uncover the mystery of what happened to these stromatolites, representative samples from each layer were taken in the current study and analyzed for possible differences in the sections with stromatolites and without stromatolites. These data will help determine the change that occurred at the event layers and will therefore provide a measure of stromatolitic sensitivity. Comparative analysis of the presence and type of microfossils (if any) between the sections with stromatolites and sections without stromatolites will aid in understanding how stromatolite morphology is affected by the species that form them. Sub-millimeter scale chemistry and structural analysis of these stromatolites will be novel contributions to the field. Studying the ecology of this particular formation, coupled with other ongoing stromatolite research, will further the use of stromatolites as biosignatures in the search for microbial life on Mars.

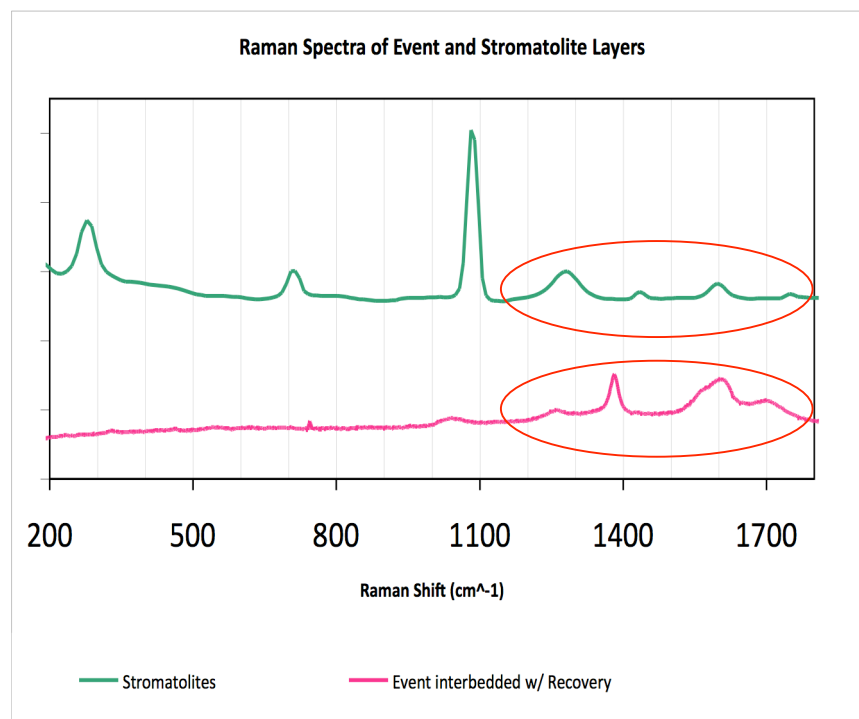


**Figure 1:** *Atypical stromatolite growth pattern: prolific growth (bottom) followed by an event (representing an environmental or biological change that killed the stromatolites) and completing the cycle with a recovery layer of normal sedimentation (top).*

## Preliminary Results

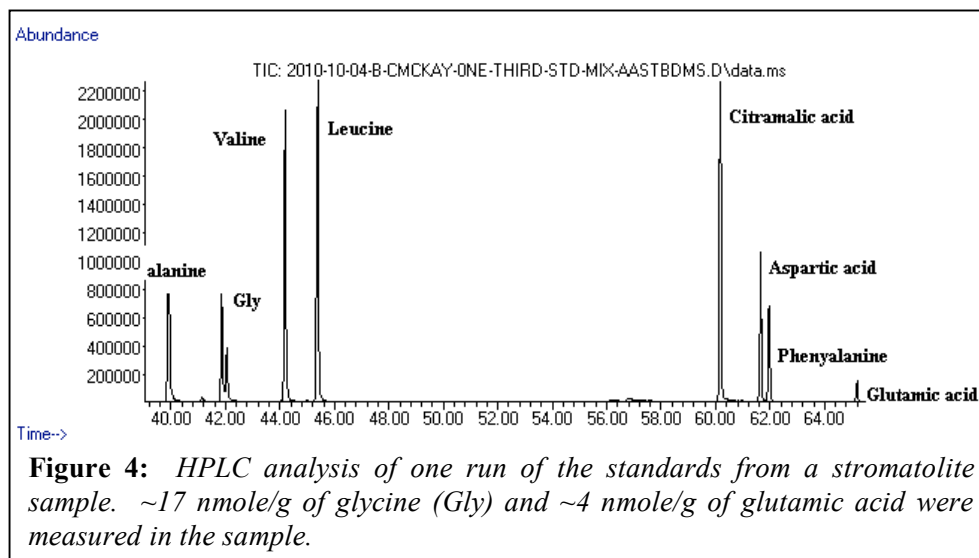
Representative samples from the Crystal Spring Formation (Figure 1) were analyzed using a 1064 nm (infrared) Raman Spectrometer and a 785 nm Raman spectrometer (Figure 2) to locate the organic content in the stromatolite, event, and recovery layers. Raman Spectroscopy is a nondestructive, in situ analysis of the unique vibrational and rotational patterns of a sample's molecular structure; using Raman scattering, a sample's molecular content, and more importantly organic content, can be illuminated.

Raman data have confirmed the presence of organic content in the Crystal Spring Formation stromatolite and event layers (Figure 2- organic peaks of  $1289\text{ cm}^{-1}$  and  $1600\text{ cm}^{-1}$  circled in red), but not the recovery layers.

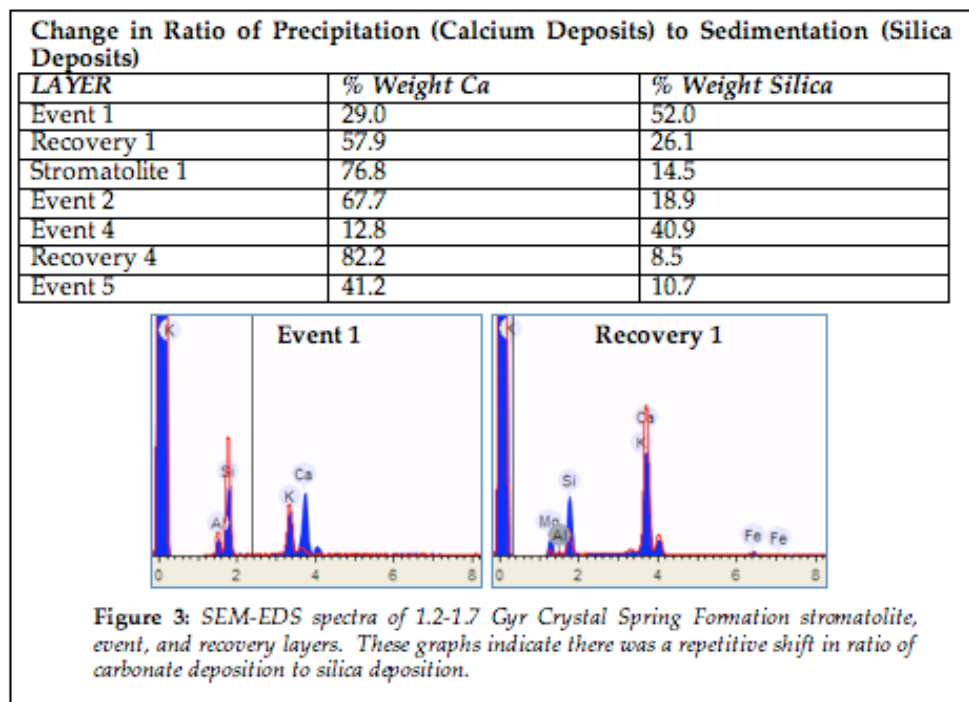


**Figure 2:** *Organic peaks ( $1289\text{ cm}^{-1}$  and  $1600\text{ cm}^{-1}$ ) of the event and stromatolite layers are circled in red. The Y-axis correlates with intensity in linear scale; the X-axis correlates to the Raman shift ( $\text{cm}^{-1}$ ).*

High-performance liquid chromatography (HPLC), a chromatographic analysis of peptide and protein structure, was used to identify and characterize amino acids in the stromatolite samples (Figure 4). The results confirmed that the stromatolite sections contained biology. Amino acid measurements of approximately 17 nmole/g of glycine ( $C_2H_5NO_2$ ) and approximately 4 nmole/g of glutamic acid ( $C_5H_9NO_4$ ) were present in the sample. Serine ( $C_3H_7NO_3$ ) was also fairly abundant in the sample. Numbers of other amino acids in the sample were difficult to obtain due to co-elution (the simultaneous emergence of multiple substances from the chromatograph column), but they all appear to near the above-concentration range.



Scanning electron microscopy with Energy-Dispersive X-ray spectroscopy (SEM-EDS) was used to analyze the samples in thin section to identify the elemental composition of the differing layers of the formation (Figure 3). From this data, it is apparent that with each successive event and recovery layer, there is a shift in the ratio of calcium deposits to silica deposits. As carbonate deposition is an indicator of precipitation and silica deposition is an indicator of sedimentation, this data suggests that there was a repeated change in the ratio of precipitation to sedimentation in the Crystal Spring Formation. Precipitation of calcite (calcium carbonate) is further indicative of a warm and shallow environment (as colder environments favor the dissolution of carbon dioxide). Moreover, continual variation in the ocean's acidity (pH) could have caused this shift in Ca/Si ratio, as precipitation of calcium carbonate can only occur at a specific pH. From this data, it is hypothesized that changes in oceanic pH and/or changes in sea level could have been the cause of the death of the stromatolites at the event layers.



## Further Research

While the Raman spectra and SEM-EDS analyses of the formation layers have provided valuable insight, our hypotheses cannot be accepted nor rejected without further information. More tests need to be run to gain a better understanding of what events could've taken place so long ago. Inductively coupled plasma mass spectrometry (ICP-MS), X-ray diffraction (XRD), amino acid dating, and optical analyses of the thin-sections are planned.

ICP-MS, a destructive method of analysis, will be used to indicate differences in the sections in terms of trace metal signatures. Trace metals of the sections might illuminate a geochemical context for the sequences in the formation. Milligram components of samples will be solubilized in solution to make plasmas, which will then be aspirated with a laser beam to vaporize the sample. A high sensitive analysis of metals and metal isotopes will then be analyzed. Three separate samples will be analyzed: a complete trace metal analysis (specifically strontium, arsenic, copper, cobalt, etc), analysis of cations, and analysis of anions.

XRD analyses will be done on representative field samples from the formation to identify the mineral composition of the event, stromatolite, and recovery layers. Data from both ICPMS and XRD analyses will help indicate whether the cause for stromatolite dormancy or extinction was a biological or environmental one.

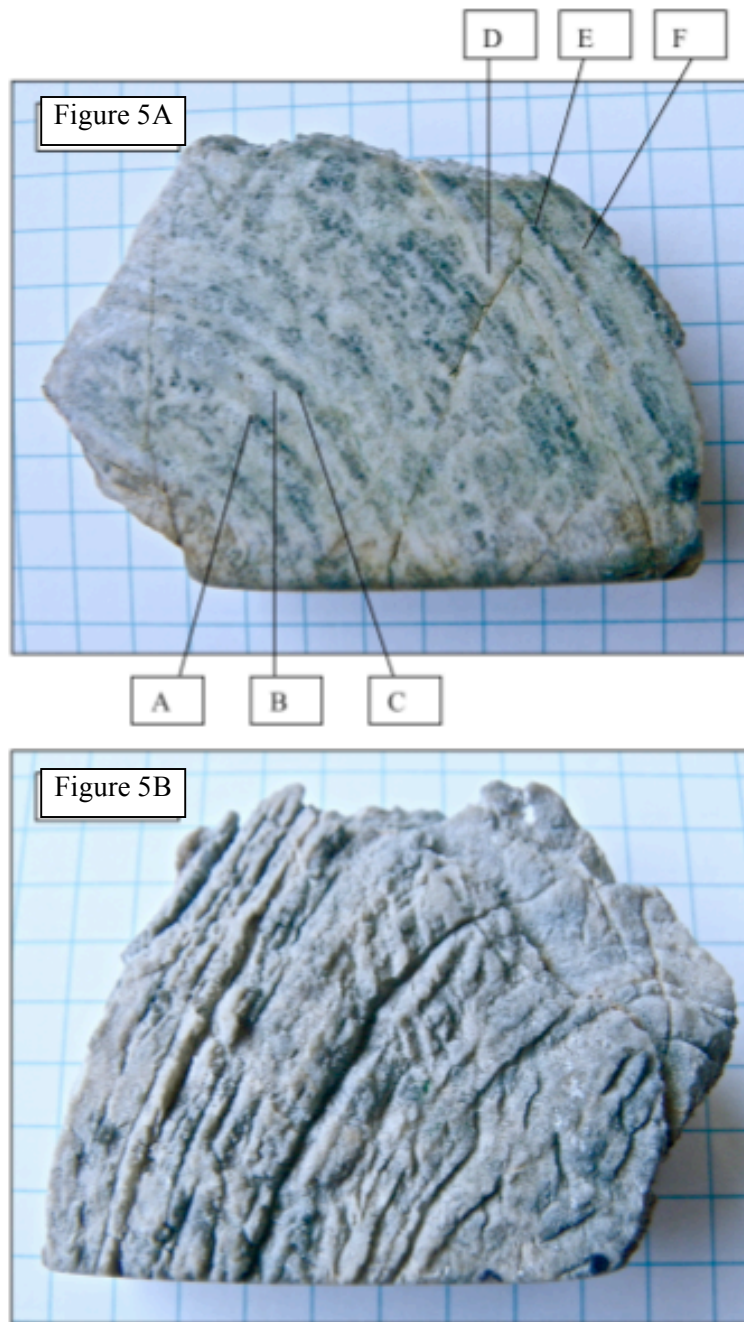
Amino acid dating will validate the proposed notion that the organic material present in the stromatolites was deposited during stromatolite formation as opposed to recent contamination. Each amino acid (except glycine) can take on two forms: "L" amino acid form and "D" amino acid form. Amino acids of living organisms only consist of the "L" form, but after death, the organism undergoes a process called racemization. Natural processes over time will shift the ratio of D/L to equilibrium [*Hare and Abelson, 1967*]. By measuring the extent of racemization of the amino acids, the relative age of the biology can be determined. If the amino acids are racemic (i.e. equal proportions of L and D forms), the amino acids are old. This would support the argument for biogenicity of the stromatolites. If the amino acids are not racemic, then the presumption would be that they are recent organic contamination.

## Discoveries and Applications

While collecting Raman spectra from the stromatolites, the 1064 nm infrared Raman spectrometer proved to be an instrumental novelty and an informative tool in characterizing ancient fossils. This instrument has shown to accurately detect organics in the 1.7 billion year old calcium carbonate stromatolites via Raman scattering.

A 1.7 billion year old stromatolite from the Crystal Spring Formation of the Mojave Desert was sliced and used for the demonstration of the Raman spectroscopic technique. Figure 5A shows the characteristic stromatolite laminae; the dark curved bands (Figure 5A- A, C, E) are organic and the lighter curved bands (Figure 5A - B, D, F) are sedimentary and inorganic. The Raman laser beam was focused at each band (Figures 6 and 7) and Raman spectra were collected sequentially. The darker bands all produced characteristic wide organic Raman peaks of 1200-1700  $\text{cm}^{-1}$  (Figure 6A), while the lighter sedimentary bands lacked those peaks (Figure 7A) [*Javaux et al., 2010*].

Identifying organic signatures in ancient samples is an informative approach to discovering extraterrestrial biology. This technique will provide extremely valuable data in analysis of Martian field samples and would be a novel and illuminating instrument to put on a rover for future Mars missions.



**Figures 5A & 5B:** *In the field one can see clear, banded structures and conical stromatolites in the rock face (Figure 5B). We obtained a small hand sample and sliced into the interior, which revealed alternating dark bands (Figure 5A). Raman spectroscopy indicates that the dark material is organic, and the lighter bands inorganic (Figures 6A & 7A).*

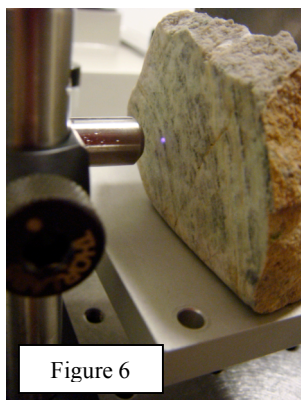


Figure 6

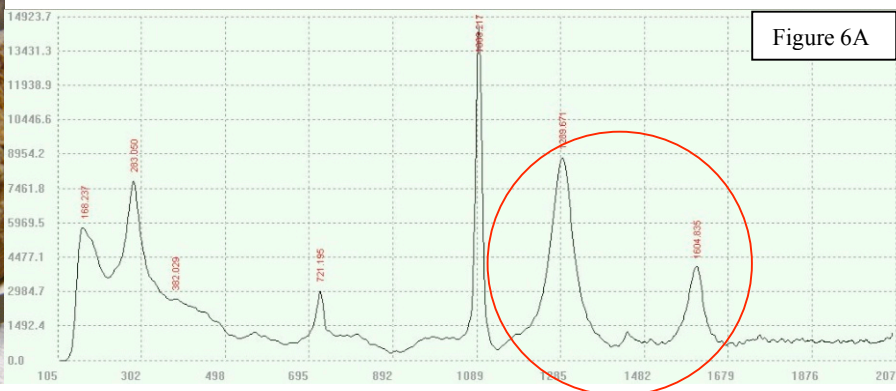


Figure 6A

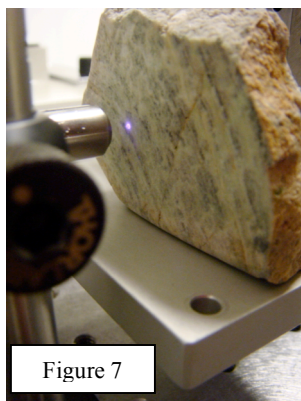


Figure 7

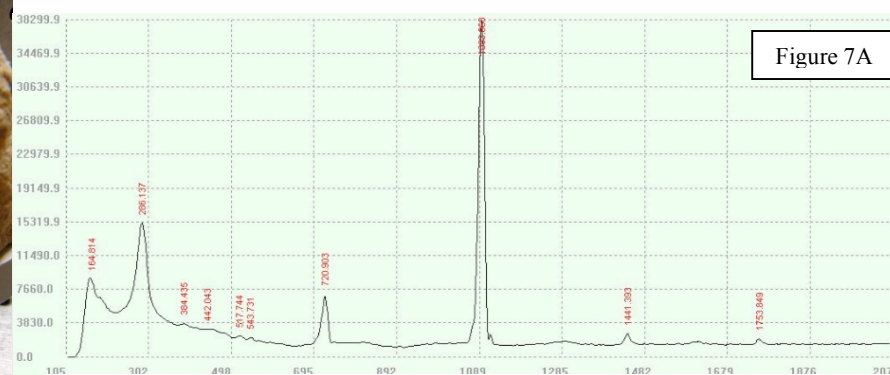


Figure 7A

Raman Shift ( $\text{cm}^{-1}$ )

**Figures 6 and 7:** Locations A, C, and E (Figure 5A) correspond to graph Figure 6A with organic peaks of  $1289 \text{ cm}^{-1}$  and  $1600 \text{ cm}^{-1}$  circled in red; Locations B, D, F (Figure 5A) correspond to the graph in figure 7A. Notice figure 7A the characteristic organic peaks are missing. The Y-axes in both graphs correlate with intensity in linear scale; the X-axes in both graphs correlate to the Raman shift ( $\text{cm}^{-1}$ ).

*This is ongoing research with Chris McKay, PhD, Bin Chen, PhD, and Zuki Tanaka.*

**Acknowledgements** I thank the NASA Astrobiology Institute (NAI) and the NASA Pennsylvania Space Grant Consortium for funding this research; NASA Spaceward Bound for the field activities; my advisors Chris McKay, Jane Dmochowski, Susanne Douglas, Gomaa Omar, and Hermann Pfeifferkorn; Bin Chen and Zuki Tanaka for Raman Spectroscopy analyses; Crystal Research Inc. for 1064 Raman spectroscopy analyses; ASL and BIN-RDI for SEM imaging and energy-dispersive X-ray analyses; George Cooper for HPLC analyses.

#### References

- Awramik SM, Corsetti FA, Shapiro R. 2000. Stromatolites and the pre- Phanerozoic to Cambrian history of the area south east of Death Valley. Bulletin of the San Bernardino County Museum 47(2):65-74.
- Cloud P, Wright LA, Williams EG, Diehl P, Walter MR. 1974. Giant Stromatolites and associated vertical tubes from upper Proterozoic noonday dolomite, Death-Valley Region, ESociety of America Bulletin 85(12):1869-82.
- Hare, P. E. and P. H. Abelson. 1967. Racemization of amino acids in fossil shells. Carnegie Institution of Washington Year Book 66 (1966-1967), pp. 526-528.
- Howell DG. 1971. A Stromatolite from the Proterozoic Pahrump Group, Eastern California. J Paleontol 45(1):48-51.
- Javaux EJ, Marshall CP, Bekker A. 2010. Organic-walled microfossils in 3.2-billion-year-old shallow-marine siliciclastic deposits. Nature 08793.
- McKay CP, Stoker CR. 1989. The early environment and its evolution on mars: Implication for life. Rev Geophys 27(2):189-214.